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**SYNTHESIS OF A
THIOPHENE-CONTAINING BISBENZIL
AND A DERIVED POLYQUINOXALINE**

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SYNTHESIS OF A THIOPHENE-CONTAINING BISBENZIL AND
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Macaione and Wentworth

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ABSTRACT

The development of polyphenylquinoxaline (PPQ) polymers as high-temperature-resistant materials has been hindered, in part, by the high cost of one resin component, 1,4-bis(phenylglyoxaloyl)benzene (PGB). A low-cost synthesis of PGB or PGB-type compounds to be substituted for PGB in the synthesis of PPQ-type polymers is therefore desirable.

This report deals with the synthesis of 1,4-bis(2-thienylglyoxaloyl)-benzene (THGB) by the benzoin condensation route in the search for a low-cost replacement for PGB, and its reaction with 3,3'-diaminobenzidine (DAB) to prepare poly(2-thienyl)quinoxaline (PTHQ). Some of the properties of the polymer have been determined and are discussed.

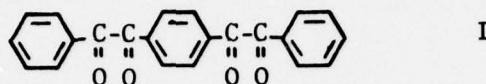
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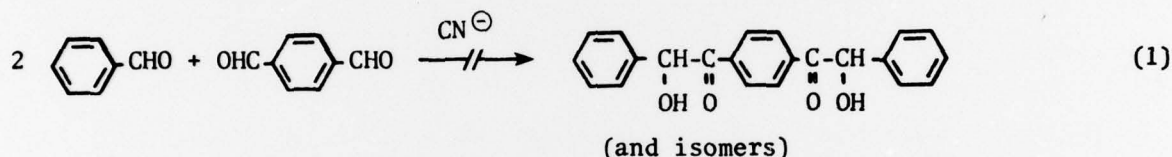
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INTRODUCTION

Since the initial report by Hergenrother and Levine¹ in 1967, polyphenylquinoxaline (PPQ) polymers have been regarded as a promising class of thermally resistant resins. The development of PPQ polymers has been hindered partly by the high cost of one resin component, 1,4-bis(phenylglyoxaloyl)benzene (PGB), I, which is prepared from expensive starting materials via a multistep synthesis.

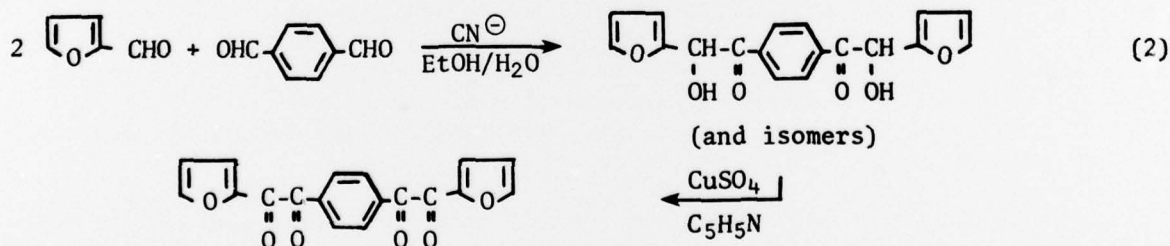


The classical approach to aromatic α -diketones, the benzoin condensation and subsequent oxidation, is an obvious direct synthetic route. However, this method has not been generally extended to the synthesis of aromatic bis- α -diketones. Attempts to condense benzaldehyde with terephthalaldehyde in the presence of cyanide ion have not been successful² (Equation 1).



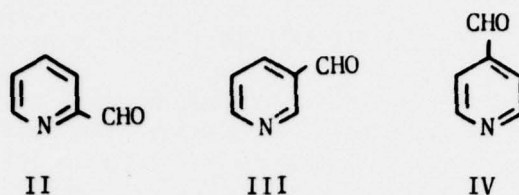
This reaction results in a mixture of products, apparently benzoin and unidentified oligomers undoubtedly arising from the self-condensation of terephthalaldehyde.

A report by Jones et al.,³ has shown that this synthetic approach can be successful with certain aldehydes as when furan-2-carboxaldehyde is condensed with terephthalaldehyde to produce, after oxidation, 1,4-bis(2-furylglyoxaloyl)-benzene (BFGB) (Equation 2).



Cherill and Wentworth⁴ reported the attempted condensation of terephthalaldehyde with the three isomeric monocarboxaldehydes of pyridine (II-IV). Although

1. HERGENROTHER, P. M., and LEVINE, H. H. *Phenyl-Substituted Polyquinoxalines*. J. Polymer Sci., v. 5, part A-1, 1967, p. 1453.
2. KRATZER, R. H., PACIOREK, K. L., and KARLE, D. W. *Modified Benzoin Condensation of Terephthalaldehyde with Benzaldehyde*. J. Organic Chem., v. 41, 1976, p. 2230. This report appeared while the present investigation was in progress.
3. JONES, R. J., VAUGHN, R. W., O'RELL, M. K., and SHEPPARD, C. H. *Development of Autoclavable Addition-Type Polyimides*. TRW Systems Group, Contract NAS 3-15834, Final Report, NASA CR-121251, 1974.
4. CHERILL, R. J., and WENTWORTH, S. E. *Attempted Synthesis of Pyridine Containing Bis- α -Diketones via the Benzoin Condensation*. Army Materials and Mechanics Research Center, AMMRC TR 76-13, April 1976.



they investigated a variety of conditions, none could be found for preparation of the desired bis-benzoin. This report describes a further extension of the benzoin route in pursuit of a low-cost replacement of PGB. Thiophene-2-carboxaldehyde has been successfully condensed with terephthalaldehyde in a classical benzoin condensation. Oxidation affords the corresponding bis- α -diketone by the cupric sulfate-hexamethylphosphoric triamide method which we previously reported for the conversion of labile benzoin to benzils.⁵ A review of the literature revealed no prior report of the synthesis of this bis- α -diketone.

EXPERIMENTAL

Materials

The thiophene-2-carboxaldehyde (Aldrich) was redistilled, in vacuo, prior to use and stored under argon with refrigeration. Terephthalaldehyde (Aldrich) was crystallized from water/ethanol prior to use. The 3,3'-diaminobenzidine (DAB) was obtained from Whittaker, R&D, San Diego, CA, recrystallized according to Hergenrother⁶ and stored under argon at -15 C. The m-cresol was distilled prior to use. All other materials were used as received.

Synthesis - 1,4-bis(2-thienylglyoxaloyl)benzene (THGB)

To a stirred solution of thiophene-2-carboxaldehyde, (6.7 g, 0.05 mole) and terephthalaldehyde (11.2 g, 0.1 mole) in ethanol was added a solution of potassium cyanide (3 g, 4.6×10^{-2} mole) in 20 ml of water. The mixture turned dark brown immediately. After refluxing with stirring for one hour, the reaction mixture was cooled to ambient temperature. With due caution, (HCN, HOOD!) 6 ml concentrated hydrochloric acid was added to the mixture which was stirred for an additional hour and chilled in an ice bath. The orange precipitate which formed was isolated, washed with ethanol, and dried in vacuo for 16 hours.

This bisbenzoin intermediate was not readily soluble in most common solvents, therefore the entire crude product was subjected to oxidation. Appropriate amounts of cupric sulfate pentahydrate and hexamethylphosphoric triamide were stirred in a flask while a stream of oxygen was bubbled through for a period of 30 minutes. The intermediate bisbenzoin was added to the mixture in one portion, and the contents of the flask turned reddish at once.

The reaction mixture was allowed to stir at ambient temperature, under oxygen, for 48 hours during which time the color changed to bright green and the solution viscosity increased. The mixture was poured into distilled water, stirred, and

5. MACAIONE, D. P., and WENTWORTH, S. E. *An Improved Method for the Synthesis of Benzils from Benzoin*. Synthesis, no. 10, October 1974, p. 716.

6. HERGENROTHER, P. M. *Poly(phenylquinoxalines)*. Macromolecular Syntheses, v. 5, 1974, p. 17.

the resulting precipitate was isolated, washed with water, air dried, and finally, dried in vacuo for 16 hours. To remove any oligomeric species present, the product was extracted for a minimum of 24 hours with chloroform and the solvent removed to yield a yellow product. Material of suitable purity for confirmation of structure was obtained by chromatography on an 18x1/2-inch column packed with silica gel with benzene/ethyl acetate (9:1) as the eluent. Such treatment resulted in a bright yellow crystalline product melting at 172 to 175 C, yield was 4.3 g (25%).

Polymerization - Poly(2-thienyl)quinoxaline (PTHQ)

Stoichiometric amounts of recrystallized 3,3'-diaminobenzidine (DAB) and 1,4-bis(2-thienylglyoxaloyl)benzene (THGB) were placed in a 3-neck flask and dissolved in sufficient distilled m-cresol to produce a 10% concentration of reactants. A stream of inert gas (argon or nitrogen) was admitted and the mixture was stirred at ambient temperature for 72 hours. Over the period of the reaction, the color of the mixture became more intense and the solution viscosity increased to such an extent that small volumes of m-cresol were added to the reaction flask periodically to maintain a fluid state. The final concentration of the reaction mixture was thus reduced to 2.5%. The reaction mixture was poured into an excess of stirred methanol and the resulting suspension gently stirred for 16 hours. The precipitated polymer was isolated by filtration through a medium glass frit, washed twice with hot methanol, extracted for 60 hours with fresh methanol to remove occluded m-cresol, and finally dried in vacuo at 85 C for 24 hours to yield a yellow-orange solid product.

RESULTS

Structural Confirmation of THGB

The structure of the presumed bis- α -diketone obtained from the oxidation of the intermediate bisbenzoin was confirmed by means of infrared spectroscopy, elemental analysis, and the proton nuclear magnetic resonance spectrum of the pure compound. The infrared spectrum was determined in KBr on a Perkin-Elmer Model 137 spectrophotometer. The bands of major interest are a doublet at 1739 cm^{-1} ($5.75\text{ }\mu$) and 1642 cm^{-1} ($6.09\text{ }\mu$) representative of the α -diketone structure. The bands at 1515 cm^{-1} ($6.60\text{ }\mu$), 1408 cm^{-1} ($7.10\text{ }\mu$), and 1348 cm^{-1} ($7.42\text{ }\mu$) are characteristic of the 2-thiophene ring-stretching vibrations.⁷ Elemental analysis was conducted by Galbraith Laboratories, Incorporated, Knoxville, TN.

Calculated for $\text{C}_{18}\text{H}_{10}\text{O}_4\text{S}_2$, molecular weight 354.4:

	%C	%H	%S
Calculated -	61.00	2.82	18.11
Found -	61.18	2.93	17.92

The proton nuclear magnetic resonance spectrum was determined with a Perkin-Elmer Model R-32 NMR spectrometer relative to TMS:

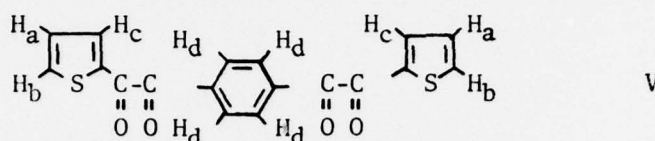
δ (ppm)

7.2	2 proton triplet
7.9	4 proton doublet
8.15	4 proton singlet

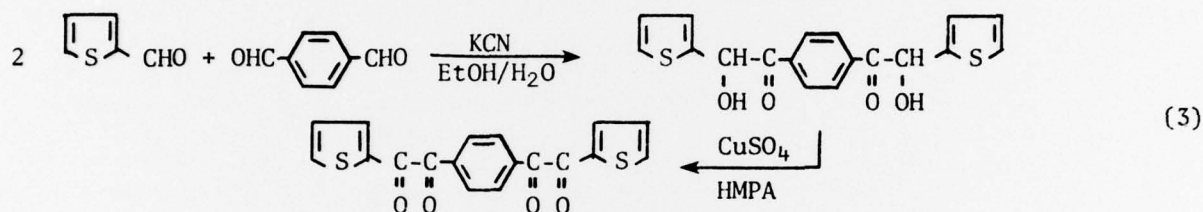
7. GRONOWITZ, S. *Recent Advances in the Chemistry of Thiophenes*. Adv. in Heterocyclic Chem., v. 1, 1963, p. 12.

In accord with spectra of known compounds, the following proton assignments were made:

H_a 7.2 ppm, $H_{b,c}$ 7.9 ppm, H_d 8.15 ppm



These results are consistent with the reaction sequence



Characterization of PTHQ

Several properties of poly(2-thienyl)quinoxaline (PTHQ) have been determined:

a. Polymer Decomposition Temperature (PDT)

The decomposition temperature of PTHQ was determined with a DuPont Model 951 thermogravimetric analyzer at a heating rate of 10 C/min in air at a flow rate of 50 cc/min. The PDT for PTHQ under these conditions is 585 C, taken as the intersection of the extrapolation of the two linear portions of the weight loss curve.

b. Isothermal Aging

Isothermal aging was conducted with the DuPont Model 951 thermogravimetric analyzer. A sample of PTHQ was held at 400 C in static air, and weight loss was measured as a function of time. Under these conditions the half-life (T_{50}) for PTHQ is approximately 10 hours.

c. Elemental Analysis

The elemental analysis of PTHQ was conducted by Galbraith Laboratories, calculated for $C_{30}H_{16}N_4S_2$:

	%C	%H	%N	%S
Calculated -	72.56	3.25	11.28	12.91
Found -	71.19	3.29	11.00	12.29

<p>Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172 SYNTHESIS OF A THIOPHENE-CONTAINING BISBENZIL AND A DERIVED POLYQUINOXALINE — Domenic P. Macaione and Stanley E. Wentworth</p> <p>Technical Report AMMRC TR 79-6, February 1979, 8 pp — illus-table, D/A Project IL162105AH84, AMCMS Code 612105.11.H84</p> <p>The development of polyphenylquinoxaline (PPQ) polymers as high-temperature-resistant materials has been hindered, in part, by the high cost of one resin component, 1,4-bis(phenylglyoxalyl)benzene (PGB). A low-cost synthesis of PGB or PGB-type compounds to be substituted for PGB in the synthesis of PPQ-type polymers is therefore desirable. This report deals with the synthesis of 1,4-bis(2-thienylglyoxalyl)benzene (THGB) by the benzoin condensation route in the search for a low-cost replacement for PGB, and its reaction with 3,3'-diaminobenzidine (DAB) to prepare poly(2-thienyl)quinoxaline (PTHQ). Some of the properties of the polymer have been determined and are discussed.</p>	<p>AD</p> <p>UNCLASSIFIED UNLIMITED DISTRIBUTION</p> <p>Key Words Synthesis (chemical) High-temperature polymers Polyquinoxaline</p>
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d. Intrinsic Viscosity

The determination of intrinsic viscosity was conducted at 30 C in *m*-cresol solution with a Cannon-Ubbelohde dilution viscometer. An intrinsic viscosity value of 1.42 dl/g was obtained for PTHQ, indicative of a polymer of substantial molecular weight.

e. Thermal Crosslinking and Torsional Braid Analysis

The thermal crosslinking and torsional braid analysis study of PTHQ was conducted in a manner identical to work which we reported earlier.⁸ The results of measuring the change in glass transition temperature ΔT_g (defined in Reference 8) as a function of the conditioning temperature for PTHQ are shown in Table 1, and graphically in Figure 1, with standard PPQ for comparison. These results clearly indicate an enhanced crosslinkability for PTHQ relative to PPQ.

Table 1. EFFECT OF THERMAL CROSSLINKING ON GLASS TRANSITION TEMPERATURE

	Conditioning Temperature (°C)	T_g (°C)	ΔT_g (°C)
PTHQ ^a	Ambient	372	-
	250	373	1
	300	380	8
	350	393	21
	400	416	44
	450	>487	>115
PPQ [†]	Ambient	350	-
	350	370	20
	400	390	40
	450	414	64

^aThis study

[†]Wentworth and Macaione

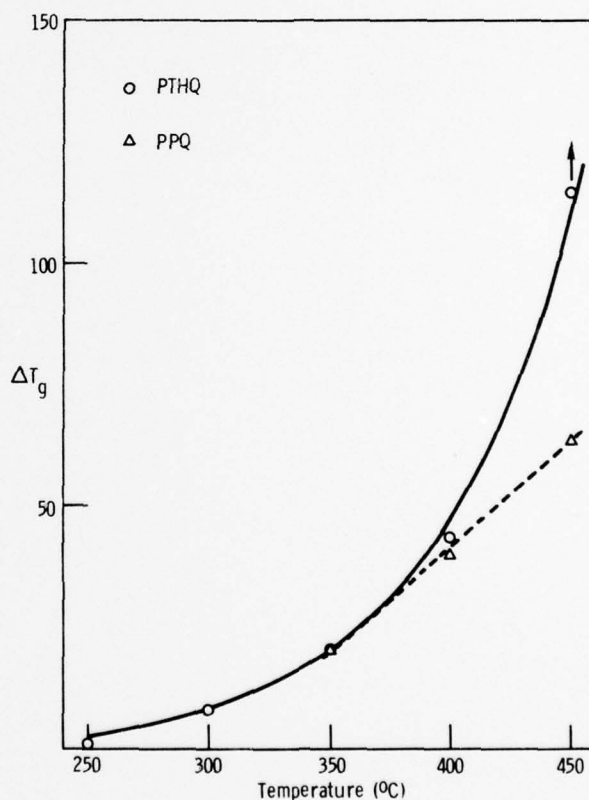


Figure 1. Change of glass transition with temperature.

8. WENTWORTH, S. E., and MACIONE, D. P. *Synthesis and Thermal Crosslinking of p,p'-Divinylbenzil Endcapped Phenylquinoxaline Oligomers*. J. Polymer Sci., Polymer Chemistry Edition, v. 14, 1976, p. 1301.

DISCUSSION

There are several points which should be stated regarding the results. First, it is to be understood that by the very nature of the benzoin condensation reaction one must postulate the formation of isomeric bisbenzoin species even though no attempt was made to isolate and identify individual isomers. Such an undertaking would be difficult under optimum conditions. The intrinsic simplicity of our synthetic approach resides in the fact that upon oxidation all isomeric forms are converted to the same tetraketone. However, the problems arising from the self-condensation of thiophene-2-aldehyde and terephthalaldehyde which can occur under the conditions of the reaction to form 2,2'-thenil and a series of oligomers, respectively, are not so easily solved. Application of the modified benzoin condensation after Kratzer et al.,² is being investigated as a means of circumventing these problems.

With regard to the characterization of the PTHQ polymer, a PDT of 585 C is slightly lower than the PDT of standard PPQ, and would indicate a somewhat lower thermo-oxidative stability for PTHQ. This is affirmed by the results of the isothermal aging experiments where the T_{50} of standard PPQ is nine times greater than that of PTHQ. Finally, although the change in T_g as a function of conditioning temperature is markedly greater for PTHQ than for PPQ, as shown in Figure 1, the results of the isothermal aging experiment indicate an insufficient thermal resistance to endow PTHQ with an extended service lifetime at elevated temperature.

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